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Colours of the Tijomel ceramic manufacture (1941-1992): characterisation of a set of ceramic colourants and glazed tiles from Decormel Materials Catalogue

As cores da fábrica de cerâmica da Tijomel (1941-1992): caracterização de um conjunto de corantes cerâmicos e dos azulejos do catálogo da Decormel

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Abstract

Tijomel was considered one of the most modern ceramic manufacturers in the Iberian Peninsula in the mid-20th century. Located at Caxarias (Ourém, Portugal), this manufacturer produced diverse ceramic-based architectural materials, from common clay bricks to sophisticated modernist azulejos. Recently members of the family of the former Tijomel Manufacture owners retrieved a collection of 33 raw materials, mostly ceramic colourants. In this study, the chemical characterisation of these ceramic colourants was performed and compared with an azulejos commercial catalogue of the same manufacturer entitled Decormel Catalogue. The recovered raw materials and azulejos were investigated using a multi-analytical approach comprising h-EDXRF and μ-XRD to obtain their elemental and mineralogical composition and HSI and colourimetry to analyse their optical properties. Results provided a glimpse of the wide variety of ceramic colourants used in mid-20th century and showed that Tijomel combined the use of traditional azulejo colourants with more recent compositions.

KEYWORDS
Azulejos
Colourants
Pigments
Ceramics

Resumo

A fábrica de cerâmica Tijomel foi considerada das mais modernas da Península Ibérica em meados do século XX. Localizada em Caxarias (Ourém, Portugal), esta fábrica produziu uma vasta gama de materiais em cerâmica, desde tijolos de barro até sofisticados azulejos modernistas. Recentemente, membros da família dos antigos proprietários da Fábrica Tijomel recuperaram um acervo de 33 matérias-primas, na sua maioria colorantes cerâmicos. Neste estudo foi realizada a caracterização destes colorantes cerâmicos e comparada com um catálogo de azulejos do mesmo fabricante, o Catálogo Decormel. Os colorantes e azulejos foram investigados usando uma abordagem multianalítica, caracterizados por h-EDXRF e μ-XRD, para obter a composição elementar e mineralógica e por câmara hiperespectral e colorimetria para determinar as propriedades ópticas. Este estudo permitiu vislumbrar a variedade de colorantes cerâmicos utilizados em meados do século XX e mostrou que a Tijomel combinava a utilização de colorantes utilizados na azulejaria tradicional com composições mais recentes.

PALAVRAS-CHAVE
Azulejos
Colorantes
Pigmentos
Cerâmica

Introduction

Azulejos are a distinctive marker of Portuguese architecture and culture [1-2]. Due to their high artistic and historical value, an increasing interest in azulejos is reflected in the growing number of studies on them, particularly in the field of conservation sciences [3-7]. Despite this growing attention, compared with other glazed ceramic productions, twentieth-century artistic ceramics have been the subject of few technical art history studies [8-9].

Post-industrial artwork differs from previous periods in its use of industrially produced raw materials, many resulting from contemporary discoveries. The characterisation of raw materials and artwork produced during this period is important for unveiling information regarding the technical art history, understanding the deterioration processes and designing dedicated conservation strategies [10-11]. Therefore researching materials catalogues can help unveil valuable technical information. A material catalogue presents a set of products that showcase the trade goods of a certain business, and may include the employed raw materials. Such catalogues were common devices for industries to publicise their products and many still exist. Because some include historical samples, materials catalogues constitute an essential reference that has not yet been fully explored analytically. Thus, investigating these raw materials allows databases of analytical results to be built up that can help identify the use of these materials in other cultural assets.

Tijomel was considered one of the most modern ceramic manufacturers in the Iberian Peninsula (Figure 1b). Located at Caxarias (Ourém) in the Leiria district in central Portugal (Figure 1a), the company was founded in 1941 under the name *Materiais para Edificação, Lda* by Júlio Redol, later changing its name to *Tijomel* (1961) and ceasing production in the 1980's [12]. Their manufactory was divided into four sections: Tijomel, Duromel, Pavimel and Decormel. This classification was based on the type of ceramic products, which ranged from common ceramic building materials like clay bricks to sophisticated modernist azulejos and mosaics [12]. In addition, the Decormel section designed and produced unusual glazed elements applied as cladding in modern Portuguese architecture (Figure 1c-d). Geraldes et al. [12] performed the first systematic research on the conservation of modernist azulejos, conducting a pioneering national survey of the application of the unique glazed ceramic elements produced by Tijomel [12]. The former Tijomel factory still display many original multi-coloured claddings, although the buildings are derelict (Figure 1b-d).

Colour in glazed ceramics is obtained by the addition of colourants to the glaze. The nomenclature and definition of ceramic colourants still lack systematisation [13-14]. In this study it was adopted the classification of colourants for both: i) soluble colourants when the chromophore ion diffuses through the fused glassy matrix and ii) stains and pigments when the colourant compounds are not dissolved within the glassy phase during firing [13-14]. Portuguese azulejos colours from the sixteenth until the mid-nineteenth century were restricted to soluble metal oxides, such as manganese, iron, copper and cobalt oxides and lead-tin or lead-antimony pigments [9]. During this period, azulejos were produced using the majolica technique, which consists of applying a white tin-opacified lead- or lead-alkali silicate glaze over the ceramic body and painting it with the colourants mentioned above in aqueous suspension directly over the raw powdered glaze [4, 7, 15]. Following the Industrial Revolution, the traditional majolica technique was partially adapted or replaced by other production methods, such as mechanical ceramic pressing, image transfer print and lithography [16]. During the 19th century, ceramic colourants that had remained unaltered for several centuries were significantly changed due to new scientific discoveries, and a wide range of colours started to be produced, such as, chromium-based pigments [17-18]. The ceramic colour industry evolved rapidly until the mid-twentieth century, with several new inorganic pigments being further developed. These included cadmium sulphide and sulphoselenides, mixed metal oxides and silicates and rutile- and zircon-based compositions [19-20]. Modern ceramic colourants have commonly been investigated in the industrial field for quality or product

development [21-24]. Likewise, ceramic colourants applied in heritage azulejos produced with the majolica technique have been partially studied [4, 6, 9]. However, few studies have focused on twentieth-century colourants in the cultural heritage field.

Recently relatives of the founder of the Tijomel ceramic manufactory found a significant collection of raw materials, primarily composed of ceramic colourants. This set of raw materials is a unique testimony to Tijomel production and provides ground information for future conservation studies. A non-invasive multi-analytical approach was applied to investigate the discovered set of Tijomel ceramic colourants, namely Handheld Energy-dispersive X-ray fluorescence (h-EDXRF), Micro-X-ray diffraction (μ-XRD), colourimetry and Hyperspectral imaging camera (Vis-NIR HSI), to characterise its elemental and mineralogical compositions and optical properties. Unlike the dyes and pigments used for other artworks, ceramic colourants are processed by firing. Therefore, the samples were analysed before and after firing using a similar approach. Additionally, the results were compared with the azulejos in a materials catalogue entitled The *Decormel Catalogue* from the Tijomel ceramics manufactory.

Figure 1. Tijomel ceramic manufacture: *a)* map of Portugal with the location of Ourém; *b)* Building of the manufacture; *c)* mixed tile patterns; *d)* patchwork with different patterns (photography: Sílvia Pereira).

Materials

The collection of ceramic raw materials and their historical background

A set of 32 Tijomel ceramic raw and colouring materials and one glaze were characterised in this study. These samples were retrieved in a well of an old house belonging to one of the Tijomel´s former owners (Figure 2a). Most materials were still in their original bags with labels; therefore, it was possible to identify their provenance and original reference (Figure 2b-c). The labels referred five different companies: Wengers, Ltd. (United Kingdom); Blythe Colour Works Ltd. (United Kingdom); Hans Barnstorf & Amp Ca Lda. (Portugal); Chambers & Amp; Ca., Lda. (Portugal) and Degussa Ltd. (Germany).

The ceramic colouring materials (ceramic colourants) were named according to the colour mentioned in the label of their original package (Figure 3 and Table 1): brown (three samples), green (four samples), red (four samples), pink (three samples), yellow (four samples), blue (three samples), violet (two samples), grey (three samples) and black (one sample). One raw material by Wengers, Lda was identified as a glaze – Aventurin Glaze 1092 G. Eleven samples were produced by Wengers, Ltd. (Table 1), a manufactory of ceramic colours, chemicals, glazes, minerals and raw materials for the ceramic industry, including pottery, tile, brick, glass and vitreous-enamelling on metal industries, located at Etruria (Stoke-on-Trent, England). This company was originally founded in Staffordshire in 1870 and ceased trading in 1984 [5]. Four of the studied ceramic colourants were produced by Blythe Colour Works (Table 1), a company located at Cresswell and specialist in colours, enamels and glazes production for the pottery industry. Blythe Colour Works was one of Europe's most advanced and successful companies in the field during the early twentieth century and operated until its closure in 2015.

Figure 2. Colourants in their original packages and details of some labels: *a)* bags with colourants after recovery from the well; *b)* label of Hans Barnstorf; *c)* bag with a label of Wenders, Ltd; *d)* bag with a label of Blythe Colour Works, Ltd; *e)* label from C. J. Chambers & Cª, Lda (photography: Joana Shearman).

Thirteen ceramic colourants were purchased at Hans Barnstorf & amp Ca Lda (Table 1). This Portuguese company was founded in 1957 in Oporto and is still in activity [6]. The company sold equipment and products for the glass and ceramic industry acquired from several international manufacturers. According to the labels, Degussa produced thirteen pigments (Hans Barnstorf had a representation of this company in Portugal). Degussa, AG (Deutsche Gold- und Silber-Scheideanstalt) was a German company initially developed for gold and silver purification, which later, in 1879, started a ceramic paints business unit after the development of a successful process for producing bright gold for decorating porcelain and glass [7]. This company was divested in August 2001 and U.S.-based Ferro Inc purchased the ceramic paints business. Three ceramic colourants were supplied by C. J. Chambers & Ca, Lda (Table 1), a Portuguese company, which we could not determine whether it was a producer or a supplier. Little information was available about this company, only that C. J. Chambers had been an employee at Ceramic Manufacture of Oporto (Empresa Cerâmica Portuense) in 1912 and later became a shareholder of a company named Chambers & Wall [25]. When colourants lacked labels, the colour reference was given according to their observed unfired colour.

Table 1. Details of the Tijomel ceramic raw materials, including colourants and glazes (manufacturer/supplier, commercial name and reference and colour according to the label).

Reference	Manufacturer/supplier	Commercial name and reference	Colour
1W	Wengers, Ltd.	Brown Rutile C2767	Brown
2W		Brown 955 GS	Brown
3W		Óxido de Vernacio C 1792	Yellow*
4W		Terraciena 2835	Brown
5W		Verde crómio 665 GS	Green
6W		Green Crystaline 1918 SM	Green
7W		Aventurin Glaze 1092 G	Light grey*
8W		Red 2540 M Majolica Glaze	Red
9W		Pink 758 GS	Pink
10W		Yellow 12	Yellow
11W		Red 5715 E	Red
12BCW	Blyte colour works, Ltd.	Black *U/G*	Black
13BCW		Chrome Green *O* W34	Green
14BCW		Crimson *U/G*	Red
15BCW		Blue 5550 GS	Blue
16H	Degussa, Ltd./ Hans Barnstorf	Cinzento Rinoceronte 25124 *Degussa*	Grey
17H		Amarelo N Gobe 23346 *Degussa*	Yellow
18H		Violeta 28010 *Degussa*	Violet
19H		2200	Violet*
20H		Azul 22704 *Degussa*	Blue
21H		Azul Cobalto *Degussa*	Blue
22H		Rosa 27702 *Degussa*	Pink
23H		Pink 27132 *Degussa*	Pink
24H		Helljadegrun 1306/XII 21534 *Degussa*	Green
25H		Cinzento azulado 25052 *Degussa*	Grey
26H		Verde Azulado 21005 *Degussa*	Bluish-Green
27H		Amarelo-Alaranjado 2336 *Degussa*	Yellow-orange
28H		Vermelho Selénio 47128 Vidrado *Degussa*	Red
29CH	CJ Chambers & Ca, Lda.	Vermelho	Red
30CH		Cinzento 61022	Grey
31CH		Verde 60148	Green
32	without label	-	Yellow*
33	without label	-	Violet*

*observed unfired colour

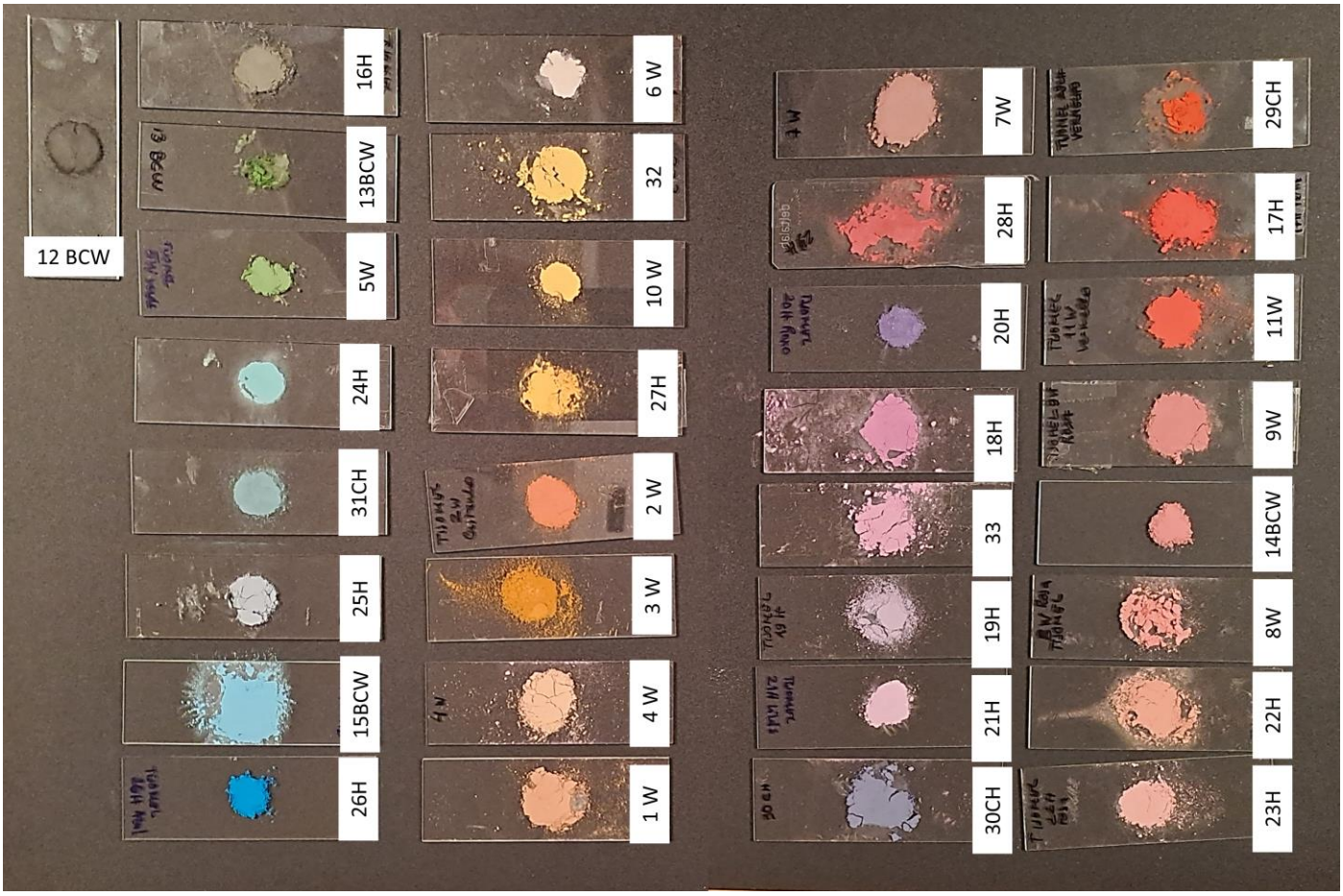

Figure 3. Samples of Tijomel raw materials, colourants and glaze on glass slides (reference according to Table 1).

Firing of the ceramic raw materials

To study the ceramic raw materials after firing, each colourant sample was dispersed in water and applied with a brush on a 2.5 × 2.5 cm square over an unfired commercial zirconium opacified lead and lime silicate glazed tile. The h-XRF analysis of the glaze of the commercial white tile showed the presence of Al, Si, K, Ca, Ba, Fe, Ni, Zn, Sr, Zr and Pb. The glaze composition may also contain boron, however this cannot be detected with the applied analytical techniques.

After applying the colourants, the tile was air-dried and fired in a Nabertherm Muffle (100 °C/h, 10 hours ramp and 40 minutes dwell at 980 °C). The selected firing cycle was optimal for the commercial glazed tile since no information was retrieved concerning the optimal firing conditions for the studied raw materials.

Material's catalogue of Decormel (Tijomel)

A set of 16 azulejos from a material's catalogue of the Decormel production line of Tijomel manufacture (hereinafter Decormel Catalogue) belonging to the Laboratório Nacional de Engenharia Civil archives (Figure 4) were analysed in this study. Only the monochrome azulejos were analysed for comparison purposes, except for the dark blue azulejo (178), because no monochrome was available (Figure 3 and Table 2). The numerical references of the analysed azulejos (with colour described in brackets) was given according to Decormel Catalogue [12]: 72 (black); 10 (vivid green); 187 (green), 48 (light green); 19 (speckled green); 116 (blue-green); 25 (red-brown); 194 (orange-brown); 155 (speckled brown); 14 (yellow); 42 (light yellow); 44 (white); 45 (light blue), 178 (blue); 28 (light grey); and 39 (grey). No sampling was allowed; therefore, only non-destructive analyses were performed directly on their surface.

Figure 4. Azulejos of the Decormel Catalogue belonging to the archive of LNEC (reference numbers added according to catalogue published by Geraldes et al. [12]).

Methods

Handheld energy-dispersive X-ray fluorescence (h-EDXRF)

To determine their elemental composition, both raw materials and azulejos were analysed with a handheld energy-dispersive X-ray fluorescence spectrometer TRACER 5i by Bruker (AXS Karlsruhe, Germany). The spectrometer is equipped with a 50 kV, 4W, Rhodium X-ray tube and a Silicon Drift Detector with a resolution of <140 eV at 250000 cps at the Mn Kα line. The operating conditions were 40 kV and 3 μA current and 180 s acquisition time. The spectra were acquired using the Bruker ARTAX v.8.0.0.476 software. Each sample was analysed in one or two spots (8 mm spot size). Before the analysis, the pigment powders were previously compressed into pellets using a hydraulic press, while the Decormel Catalogue azulejos were analysed directly on the surface.

Micro-X-ray diffraction (μ-XRD)

The mineralogical composition of the raw materials (before and after firing) and Decormel Catalogue azulejos was determined with a D8 Discover micro X-ray diffractometer by Bruker (AXS Karlsruhe, Germany) with CuKα radiation tube operating at 40 kV and 40 mA. The XRD peaks were measured between 5° and 75° 2θ, with 1 s counting time per point. The microanalyses mode with a 1 mm diameter of the beam was useful for analysing locally the small azulejos surface in a non-destructive practice. The Bruker EVA software was used for the identification of the crystalline phases using Powder Diffraction Database (PDF -ICDD, International Centre for Diffraction Data) as reference.

Colorimetry

Colour coordinates and diffuse reflectance spectral curves of the fired raw materials and the Decormel Catalogue azulejos in the visible range (380-750 nm) were acquired with a Lovibond colorimeter, equipped with an integrating sphere in the following conditions: diffuse illumination 8◦ viewing (in agreement with the CIE publication No. 15.2 Colorimetry), SCE and Illuminant/Observer D65/10°. The aperture size used was USAV (Ø=4 mm). Results are the average of three measurements taken on each painted area.

Hyperspectral imaging camera (HIS)

Hyperspectral imaging (HSI) or Vis-NIR reflectance spectroscopy is a non-invasive technique that has been applied to investigate colourants on stained glass and ceramics [26-27]. With this goal, a Specim IQ mobile hyperspectral camera by Specim Ltd (Oulu, Finland) was used to acquire hypercubes of the raw materials (before and after firing) and azulejos from the Decormel Catalogue. The built-in Si-CMOS sensor collects data in the spectral region ranging from 400 to 1000 nm in 204 bands with a spectral resolution of 3 nm to generate 512 × 512 pixel acquisition areas (hypercubes). The Specim IQ device performs background correction automatically, and all assays were recorded by including a white reference panel (Specim Ltd) for colour calibration with the build-in software for in situ data acquisition, validation and conversion to apparent reflectance. For the illumination, a halogen lamp (1000 W, temperature colour 3200 K) was placed at a ca. 2 m distance from the samples. The lighting source was not projected directly onto the object but onto a white scattering surface to draw a 40° angle sample-scattering surface-lamp to ensure diffuse illumination to the object while avoiding specular reflectance. Three representative reflectance spectra were obtained for each sample from the acquired hypercubes using ENVI analysis software (ENVI Classic 5.3, Exelis VIS, Boulder, CO).

Results

Characterisation of the ceramic colourants

The ceramic colourants were first investigated in the raw form by exploring their chemical and mineralogical composition, as well as their optical properties in the Vis-NIR region, by reflectance spectroscopy (HSI) and colorimetry. After applying the colourants on a glaze tile and firing it, their colour, mineralogical composition and optical properties were re-evaluated (Figure 5 and Figure 6). The colourant materials' elemental composition (Table 2) was not re-evaluated after firing since the major changes caused by firing mainly relate to their incorporation into the tile's base glaze.

Through the elemental composition analysis of the colourants (Table 2), it was possible to identify elements and conjecture about their possible role in the colourant powder, either as a colour agent, opacifier or as an element related to the composition of the structural glaze matrix. In the glaze composition, the various elements can have different roles, such as network former, which by themselves can form a glass (e.g. SiO_2, B_2O_3), as fluxes (those

materials that lower the melting temperature, e.g. Na_2O, K_2O, PbO) and as stabilisers (compounds that display an intermediate character between the network former and fluxes, e.g. Al_2O_3) [28]. Al and Si were identified in most pigments, and often K and Ca, which are all common constituents of a glassy phase (Table 2). Pb which may also be related to a glassy matrix, was also detected in several samples (Table 2), as were tin and zirconium which are commonly used for opacification of the glaze through the precipitation of cassiterite [29] and zircon [30]. The selected analytical set-up did not permit the identification of B on the glazes, although it was probably present. The colourant samples (7W) referenced as a glaze (Table 1), presented borax in the mineralogical composition.

Table 2. List of elements detected in the ceramic raw materials (probable chromophore elements in bold) and Decormel Catalogue azulejos by h-EDXRF analysis.

Samples	Colour	Reference	Elements
Tijomel raw materials (powder)	Black	12BCW	Al, Si, K, Ca, Ti, **Cr**, Mn, **Fe**, **Co**, **Ni**, Cu, **Zn**, Pb
	Blue	15BCW	**Si**, P, **V**, Fe, **Zr**
		20H	Al, **Si**, K, Ca, Fe, **Co**, Zn
		21H	Al, **Si**, K, Ca, Fe, **Co**, Zn, Pb
	Brown	1W	Al, Si, K, Ca, **Ti, Cr**, Fe, Ni, Zr, **Nb**
		2W	Al, Si, **Cr**, **Fe**, **Zn**, **Sn**
		4W	Al, Si, K, Ca, **Ti**, **Cr**, Fe, Ni, Zn, Zr, **Nb**, Pb
	Green	5W	Al, Si, K, Ca, Ti, **Cr**, Fe, **Co**, **Zn**, Sn, Pb
		6W	Al, Si, P, K, Ca, Ti, **Cr**, **Fe**, Ni, **Cu**, Zr, Pb
		13BCW	Al, Ca, **Cr**, Fe, Ni, Zr
		26H	Al, Si, Ca, **Cr**, Fe, **Co**, Ni
		24H	**Si**, **V**, Fe, Ni, **Zr**
		31CH	Al, Si, S, K, Ca, Ti, **Cr**, Fe, **Co**, Ni, Cu, **Zn**
	Grey	16H	Al, Si, S, K, **Mn**, **Fe**, **Co**, **Ni**, **Sn**
		25H	Al, Si, **Cr**, **Fe**, **Co**, **Ni**, Pb, Zr, **Sn**, Pb
		30CH	Al, Si, K, Ca, **Cr**, **Mn**, **Fe**, **Co**, **Ni**, **Zn**, **Sn**
	Pink	9W	Al, Si, **Ca**, Ti, **Cr**, Fe, Co, Ni, Zn, **Sn**, Pb
		22H	**Al**, Si, K, Ca, Ti, Cr, **Mn**, Fe, Ni, Zn, Zr, Sn, Pb
		23H	Al, Si, **Ca**, Ti, **Cr**, Fe, Co, Ni, Zn, **Sn**, Pb
	Red	7W	Al, Si, **Ca**, Ti, **Cr**, Fe, Ni, Zn, Cd, **Sn**, Pb
		8W	Al, Si, **S**, K, Ca, Ti, Cr, Mn, Fe, Ni, Zn, **Se**, Zr, **Cd**, Sn, Pb
		11W	Al, Si, **S**, Ba, Fe, Ni, Zn, **Se**, Zr, **Cd**, Ba, Pb
		28H	Al, Si, **S**, K, Ca, Ti, Fe, Ni, Zn, **Se**, **Cd**, Zr, Pb
		29CH	Al, Si, **S,** K, Ca, Ti, Cr, Mn, Fe, Ni, Zn, **Se**, **Cd**, Zr, Pb
		14BCW	Al, Si, **Ca**, **Cr**, Fe, **Sn**, Pb
	Violet	18H	Al, Si, S, K, Ca, Ti, **Cr**, Mn, Fe, Co, Ni, Zn, Zr, **Sn**, Pb
		19H	Al, **Si**, S, K, Ca, Ti, Mn, Fe, **Co**, Ni, Zn, Pb
		33	Al, Si, K, Ca, Ti, **Cr**, Mn, Fe, Co, Ni, Zn, **Sn**, Pb
	Yellow	10W	Al, Si, K, Ca, Fe, Ni, Zn, Zr, Cd, Sn, **Sb**, **Pb**
		17H	Al, Si, **S**, K, Ca, Fe, Ni, Zn, **Se**, Rb, Zr, **Cd**, Sn, Pb
		27H	Al, Si, K, Ca, Fe, Ni, Zn, Rb, Sr, Zr, Sn, **Sb**, **Pb**
		32	Al, Si, Ca, **V**, Fe, **Sn**, Pb
	-	3W	Al, Si, S, **V**, Fe, Sn
Decormel Catalogue (Azulejos)	Black	72	Al, Si, K, Ca, Ti, **Cr**, **Mn**, **Fe**, **Co**, Ni, Cu, **Zn**, Rb, Sr, Zr, Sn, Pb
	Green	10	Al, Si, K, Ca, Ti, **Cr**, Fe, Ni, **Zn**, Rb, Sr, Zr, Cd, Sn, Pb, Ba
		187	Al, Si, K, Ca, Ti, **Cr**, Fe, Ni, **Zn**, Rb, Sr, Zr, Cd, Sn, Pb, Ba
		19	Al, Si, K, Ca, Ti, Cr, Fe, Ni, **Cu**, Zn, As, Zr, Sn, Sb, Pb
		48	Al, Si, K, Ca, Ti, **V**, Fe, Ni, Zn, Rb, Sr, **Zr**, Cd, Sn, Pb, Ba
	Red-brown	25	Al, Si, K, **Ca**, **Ti**, Cr, Fe, Ni, Cu, Zn, Rb, Sr, Zr, Cd, **Sn**
	Orange-brown	194	Al, Si, K, Ca, Ti, **Cr**, **Fe**, Ni, Cu, **Zn**, Rb, Sr, Zr, Cd, **Pb**
	Brown	155	Al, Si, K, Ca, Ti, **Cr**, **Fe**, Ni, Cu, **Zn**, Rb, Sr, Zr, Cd, **Sn**, **Sb**, **Pb**
	Yellow	14	Al, Si, K, Ca, Fe, Ni, Zn, Zr, Cd, **Sn**, **Sb**, **Pb**
		42	Al, Si, P, K, Ca, Ti, **V**, Fe, Cu, Zn, Zr, Cd, **Sn,** Pb
	White	44	Al, Si, P, K, Ca, Fe, Ci, Zn, **Zr**, Cd, Sn, Sb, Pb
	Blue	45	Al, Si, K, Ca, **V**, Fe, Co**,** Cu, Ni, Zn, **Zr**, Sn, Sb, Ba, Pb
		178	Al, Si, K, Ca, Fe, **Co**, Ni, **Zr**, **Sn**, Ba, Sn, Pb
		116	Al, Si, K, Ca, Ti, **V**, Fe, Ni, **Cu**, Zn, **Zr**, Pb
	Grey	28	Al, Si, K, Ca, Ti, **Cr**, **Mn**, **Fe**, **Co**, **Ni**, **Cu**, **Zn**, Rb, Sr, Zr, Sn, Pb
		39	Al, Si, K, Ca, Ti, **Cr**, **Mn**, **Fe**, **Co**, **Ni**, **Cu**, **Zn**, Rb, Sr, Zr, Sn, Pb

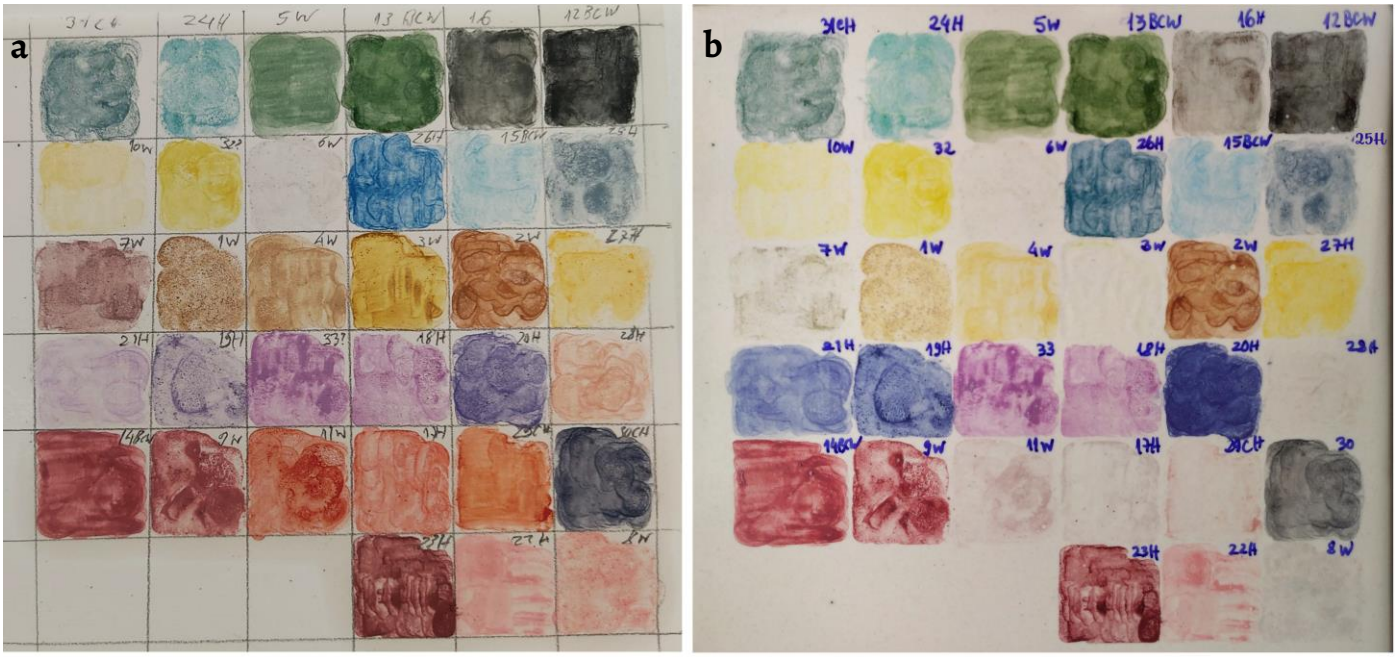

Figure 5. Tijomel raw materials, colourants and glaze, tested on a commercial white tile: *a)* before firing; *b)* after firing.

Considering that the base glaze composition and firing conditions can affect the colour outcome, firing the discovered colourant materials allowed us to evaluate their plausible final colour and mineralogical composition (Table 3). Visual observation showed that some of the discovered colourants suffered substantial change after firing (Figure 5).

The mineralogical composition of the raw materials showed a wide range of different mineral phases (Table 3). The mineralogical composition of all the colourants applied on the commercial tile after firing presented zircon ($Zr(SiO_4)$, PDF 80-1807), quartz (SiO_2, PDF 78-2315) and sometimes cristobalite (SiO_2, PDF 82-0512), which are constituents of the commercial white glaze and therefore were not included in the list of mineral phases (Table 3), except when zircon was believed to be related to the pigment´s mineral phase.

The final identification of the type of ceramic colourants relied on a combination of the results provided by the elemental composition, mineralogical profile and optical properties. The analysis of the results and discussion of the analysed materials are grouped by the colour according to the reference colour described in their original labels (Table 1).

Table 3. Mineral phases identified on the Tijomel ceramic raw materials, before firing (powders) and after firing over a white tile, and on the azulejos of the Decormel Catalogue, obtained by XRD analysis.

Samples	Colour	Reference	Chromophore	Mineral phases and chemical formula (corresponding PDF card number in footnote[1])	
				Before firing	After firing
Ceramic raw materials	Glaze	7W	-	Borax ($Na_2B_4O_7{\cdot}10H_2O$) Hematite (Fe_2O_3)	Wuestite (FeO) Hematite (Fe_2O_3)
	Black	12BCW	Cr, Fe, Co, Ni, Zn	Cochromite ($CoCr_2O_4$) Trevorite, syn ($NiFe_2O_4$) Zincococchromite ($ZnCr_2O_4$) Hematite (Fe_2O_3)	Cochromite ($CoCr_2O_4$/$CoO{\cdot}Cr_2O_3$) Zincococchromite ($ZnCr_2O_4$)
	Brown	1W	Ti, Cr, Nb	Rutile (TiO_2)	Rutile (TiO_2)
		2W	Cr, Fe, Zn, (Sn)	Magnetite (Cr-bearing) (Fe_2O_3) Chromite, syn ($Fe^{+2}Cr_2O_4$) Gahnite, syn ($ZnAl_2O_4$/ZnO, PDF 05-0669) Cassiterite (SnO_2, PDF 21-1250)	Zincococchromite ($ZnCr_2O_4$) Hematite (Fe_2O_3) Cassiterite, syn (SnO_2)
		4W	Ti, Cr, Nb, Zr	Rutile (PDF 89-0552) Zircon ($Zr(SiO_4)$) Quartz (SiO_2) Chromium oxide (Cr_3O_4)	Rutile (TiO_2)
	Blue	15BCW	Si, V, Zr	Zircon ($Zr(SiO_4)$) Quartz (SiO_2)	

			Cristobalite (SiO_2) Baddeleyite, syn (ZrO_2)	
	20H	Co	Quartz (SiO_2) Olivine, syn ($Co_2(SiO_4)$)	Olivine, syn ($Co_2(SiO_4)$)
	21H	Co	Olivine, syn ($Co_2(SiO_4)$)	
Green	5W	Cr, Co	Eskolaite (Cr_2O_3, PDF 74-0326) Quartz (SiO_2) Cochromite ($CoCr_2O_4$) Kaolinite ($Al_2Si_2O_5(OH)_4$)	Eskolaite (Cr_2O_3) Cristobalite (SiO_2) Anorthite, ordered ($CaAl_2Si_2O_8$)
	6W	Cr, Co, Cu	Hydrocerussite ($Pb_3(CO_2)_2(OH)_2$) Cerussite ($PbCO_3$) Quartz (SiO_2)	
	13BCW	Cr	Eskolaite (Cr_2O_3)	Eskolaite (Cr_2O_3)
	24H	V, Zr	Zircon ($Zr(SiO_4)$) Quartz (SiO_2) Cristobalite (SiO_2) Baddeleyite (ZrO_2)	Zircon ($Zr(SiO_4)$)
	26H	Cr, Co	Quartz (SiO_2) Cobalt oxide (Co_3O_4) Aluminium Oxide Chromium ($(Al.948Cr.052)_2O_3$)	Cobalt chromium oxide ($CoCr_2O_4$)
	31CH	Cr, Co, Ni, Zn	Zincocochromite ($ZnCr_2O_4$) Cobalt chromium oxide ($CoCr_2O_4$) Willemite ($Zn_2(SiO_4)$) Cobalt oxide (Co_3O_4)	Zincocochromite ($ZnCr_2O_4$) Cobalt chromium oxide ($CoCr_2O_4$)
Grey	16H	Mn, Fe, Co, Ni	Cassiterite, syn (SnO_2) Spinel, syn $(Mn0.718Fe0.402Ti0.88)(Ti0.12Fe0.316Mn0.564)O_4$) Bunsenite (NiO)	Cassiterite, syn (SnO_2)
	25H	Co	Quartz (SiO_2) Cassiterite, syn (SnO_2) Olivine, syn ($Co_2(SiO_4)$)	Cassiterite, syn (SnO_2)
	30CH	Cr, Mn, Fe, Co, Ni, Zn	Corundum, syn (Al_2O_3) Gahnite ($ZnAl_2O_4$/ZnO) Franklinite, syn ($ZnFe_2O_4$) Cuprospinel, syn (Cu.86Fe2.14°4)	Anorthite, ord ($CaAl_2Si_2O_8$)
	3W	V	Shcherbinaite (V_2O_5, PDF 41-1426)	
Pink	9W	Cr, Sn	Malayaite ($CaSn(SiO_4)O$) Cassiterite, syn (SnO_2) Quartz (SiO_2)	Malayaite ($CaSn(SiO_4)O$)
	22H	Al, Mn	Corundum, syn (Al_2O_3) Kaolinite ($Al_2Si_2O_5(OH)_4$) Quartz (SiO_2)	Corundum, syn (Al_2O_3) Anorthite, ord ($CaAl_2Si_2O_8$)
	23H	Cr, Sn	Malayaite ($CaSn(SiO_4)O$) Cassiterite, syn (SnO_2) Quartz (SiO_2)	Malayaite ($CaSn(SiO_4)O$) Cassiterite, syn (SnO_2)
Red	8W	S, Se, Cd, Sn	Cadmium Selenide Sulfide (Cd10S5.71Se4.29) Quartz (SiO_2)	
	11W	S, Se, Cd	Cadmium Selenide Sulfide (Cd10S5.71Se4.29) Cadmium Selenide Sulfide (CdS0.75Se0.25) Quartz (SiO_2)	
	28H	S, Se, Cd	Cadmium Selenide Sulfide (Cd10S5.71Se4.29) Quartz (SiO_2)	
	29CH	S, Cd	Cadmium Selenide Sulfide (Cd10S5.71Se4.29) Cadmium Selenide Sulfide (CdS0.75Se0.25, PDF 49-1459) Quartz (SiO_2)	
	14BCW	Cr, Sn	Malayaite ($CaSn(SiO_4)O$) Cassiterite, syn (SnO_2)	Malayaite ($CaSn(SiO_4)O$)
Violet	18H	Si, Cr	Cassiterite, syn (SnO_2)	Cassiterite, syn (SnO_2)
	19H	Si, Co	Olivine, syn (Co_2SiO_4) Kaolinite ($Al_2Si_2O_5(OH)_4$) Quartz (SiO_2)	Feldspar
	33	Si, Cr, Sn	Cassiterite, syn (SnO_2)	Cassiterite, syn (SnO_2)
Yellow	10W	Pb, Sb	Bindheimite, syn ($Pb_2Sb_2O_7$) Cassiterite, syn (SnO_2) Baddeleyite (ZrO_2) Antimony oxide -hydrate ($Sb_2O_5 \cdot 2.5H_2O$)	Bindheimite, syn ($Pb_2Sb_2O_7$)
	17H	Se, Cd	Cadmium Selenide sulfide (Cd10S5.71Se4.29)	Cadmium Selenide sulfide (Cd10S5.71Se4.29)
	27H	Pb, Sb	Bindheimite, syn ($Pb_2Sb_2O_7$) Cassiterite, syn (SnO_2)	Bindheimite, syn ($Pb_2Sb_2O_7$) Cassiterite, syn (SnO_2)

				Litharge (PbO) Cerussite ($PbCO_3$) Massicot (PbO) Microclina maximum	Litharge, syn (PbO)
		32	V, Sn	Cassiterite, syn (SnO_2) Cristobalite (SiO_2) Lead oxide (Pb_2O_3) Baddeleyite (ZrO_2) Anhydrite, syn ($CaSO_4$)	Cassiterite, syn (SnO_2) Zircon ($Zr(SiO_4)$)
Decormel Catalogue (azulejos)	Black	72	Cr, Mn, Fe, Co, Ni, Zn		Quartz (SiO_2) Zircon ($Zr(SiO_4)$) Spinel
	Green	10	Cr		Quartz (SiO_2) Zircon ($Zr(SiO_4)$)
		187	Cr		Quartz (SiO_2) Zircon ($Zr(SiO_4)$)
		19	Co, Cu		Quartz (SiO_2) Zircon ($Zr(SiO_4)$) Eskolaite, syn (Cr_2O_3)
		48	Co, Zn		Quartz (SiO_2) Zircon ($Zr(SiO_4)$)
	Brown-red	25	Cr, Ca, Sn		Malayaite ($CaSn(SiO_4)O$)
	Brown-orange	194	Cr-Fe- Zn, Zr		Quartz (SiO_2) Zircon ($Zr(SiO_4)$) Aluminian Chromite, syn $Fe(Al,Cr)_2O_4$, PDF 01-1129 spinel(Cu, Ni, Mn)$CuNi_{0.5}Mn_{1.5}O_4$ Syn PDF 80-2185
	Brown	155	Cr, Fe, Zn, Sb-Pb		Quartz (SiO_2) Zircon ($Zr(SiO_4)$) Malayaite ($CaSn(SiO_4)O$) Cassiterite, syn (SnO_2)
	Yellow	14	Sn, Sb, Pb		Quartz (SiO_2) Zircon ($Zr(SiO_4)$) Lead tin antimony oxide ($Pb_2(Sn, Sb)O_{6.5}$) Cassiterite, syn (SnO_2)
		42	V, Sn		Quartz (SiO) Zircon ($Zr(SiO_4)$) Cassiterite (SnO_2)
	White	44	Zr		Quartz (SiO_2) Zircon ($Zr(SiO_4)$)
	Blue	45	Si, V, Zr		Quartz (SiO_2) Zircon ($Zr(SiO_4)$) Cassiterite (SnO_2)
		178	Co		Quartz (SiO_2) Zircon ($Zr(SiO_4)$) Cassiterite (SnO_2)
		116	V-Zr, Cu		Quartz (SiO_2) Zircon ($Zr(SiO_4)$) Cassiterite (SnO_2)
	Grey	28	Cr, Mn, Fe, Co, Ni, Zn		Quartz (SiO_2) Zircon ($Zr(SiO_4)$) Cassiterite (SnO_2)
		39	Cr, Mn, Fe, Co, Ni, Zn		Quartz (SiO_2) Zircon ($Zr(SiO_4)$) Cassiterite (SnO_2) Chromite Al-rich
	Commercial white tile				Quartz (SiO_2) Zircon ($Zr(SiO_4)$)

[1]Mineral phase and corresponding PDF card reference: Borax ($Na_2B_4O_7{\cdot}10H_2O$, PDF 24-1055); Hematite (Fe_2O_3, PDF 33-0664); Wuestite (FeO, PDF 02-1180); Cochromite ($CoCr_2O_4$, PDF 78-0711); Trevorite, syn ($NiFe_2O_4$, PDF 44-1485); Zincocochromite ($ZnCr_2O_4$, PDF 22-1107); Baddeleyite, syn (ZrO_2, PDF 37-1484); Olivine, syn ($Co_2(SiO_4)$, PDF 87-0053); Rutile (TiO_2, PDF 21-1276); Magnetite (Cr-bearing) (Fe_2O_3, PDF 88-0866); Chromite, syn ($Fe^{+2}Cr_2O_4$, PDF 34-0140); Cobalt chromium oxide ($CoCr_2O_4$, PDF78-0711), Cobalt oxide (Co_3O_4, PDF 80-1537); Gahnite, syn ($ZnAl_2O_4$/ZnO, PDF 05-0669); Cassiterite (SnO_2, PDF 21-1250); Chromium oxide (Cr_3O_4, PDF 12-0559); ZnO Zincite, syn (PDF 36-1451); Titanite ($CaTiSiO_5$ PDF 73-2066); Eskolaite (Cr_2O_3, PDF 74-0326); Quartz (SiO_2); Anorthite, orderred ($CaAl_2Si_2O_8$, PDF 41-1486); Hydrocerussite ($Pb_3(CO_3)_2(OH)_2$, PDF 10-0410), Cerussite ($PbCO_3$, PDF 47-1734), Tenorite (CuO, PDF 48-1548), Galaxite cobaltian, syn ($Mn_{0.9}Co_{0.1}Al_2O_4$, PDF 76-0072); Cobalt Manganese Spinel (Co_2MnO_4, PDF 01-1130); Spinel, syn ($Mn_{0.718}Fe_{0.402}Ti_{0.88})(Ti_{0.12}Fe_{0.316}Mn_{0.564})O_4$, PDF 82-1298); Bunsenite (NiO, PDF 02-1216); Corundum, syn (Al_2O_3, PDF 42-1468); Aluminium Oxide Chromium $(Al_{.948}Cr_{.052})_2O_3$, PDF 71-0958); Franklinite, syn ($ZnFe_2O_4$, PDF 22-1012); Aluminian Chromite, syn ($Fe(Al,Cr)_2O_4$, PDF 01-1129); spinel (Cu, Ni, Mn), syn ($CuNi_{0.5}Mn_{1.5}O_4$, PDF 80-2185); Malayaite ($CaSn(SiO_4)O$, PDF 86-0928); Cadmium Selenide Sulfide ($Cd_{10}S_{5.71}Se_{4.29}$, PDF 40-0838); Cadmium Selenide Sulfide ($CdS_{0.75}Se_{0.25}$, PDF 49-1459); Bindheimite, syn ($Pb_2Sb_2O_7$, PDF 74-1354); Litharge (PbO, PDF 01-0824), Lead tin antimony oxide (PDF 78-1549); Kaolinite 2M ($Al_2Si_2O_5(OH)_4$, PDF 75-0938).

Black, grey and brown colours

The black pigment 12BCW was composed of a mixture of transition metals, including Cr, Fe, Co, Ni and Zn (Table 3). The proposed mineralogical composition should be a spinel structure close to cochromite, trevorite or zincochromite (Table 3), although the exact identification of the mineral phase was not possible (Table 3). Spinel structures are usually cubic oxides formed by eight tetrahedral and four octahedral sites that coordinate oxygen atoms [31]. Their generic formula is $RO.R_2O_3$, where RO can be – MgO, ZnO, NiO, CoO, CdO, MnO or FeO while R_2O_3 can be Cr_2O_3, Al_2O_3 or Fe_2O_3 [31]. Black ceramic colourants are usually obtained either by pigments or stains with spinel structure and/or mixtures of transition metal oxides [32]. The mixture of multiple transition metals explains the difficulty in identifying their exact mineral phase [23, 32]. The characterisation of the microstructures and elemental distribution could provide further information regarding the colourant. An example of the black pigment reflectance spectra is given in Figure 6, which shows that the black pigment absorbed almost all the visible wavelength range, as expected. However, it presented a higher transmission in the red region.

The grey pigments (catalogue reference numbers 16H, 25H and 30CH) were formed by a mixture of the same type of elements and a similar structure identified in black 12BCW (i.e., transition element spinels) to which white cassiterite (SnO_2) had been added (Table 3). Due to the addition of a white colourant, the samples presented higher reflectance values in the visible range, as can be observed in sample 25H in Figure 6. The different grey pigments had some variations regarding their composition: sample 30CH had mainly Cr, Co and Zn; 16H had Mn, Co and Ni; and 25H had Fe, Co and Ni. In the reflectance spectra of sample 30CH, in Figure 6, the Co^{2+} absorption bands are evident, at around 540, 585 and 620 nm [30] before firing, suggesting a more significant influence of cobalt on the final colour.

The brown pigment is a Fe-Cr-Zn spinel (2W). Pigment 2W presented high concentrations of three transition metals Cr, Fe and Zn (Table 2), and a crystalline structure similar to spinel (Zn, Fe) or chromite (Table 3). According to the literature variation in the ratio of Fe and Zn can be used to change black ceramic pigments into brown [32]. Two other brown pigments (1W and 4W) were totally different, being identified as rutile brown pigments of the chrome niobium titanium rutile [$(Ti,Cr,Nb)O_2$] type. These three elements, Cr, Nb and Ti were identified by XRF (Table 2) and rutile was the main mineral phase identified by XRD, both in the raw and fired samples (Table 3). This brown pigment is obtained by doping rutile (TiO_2) with Cr and Nb ions through a reaction at high-temperature calcination [33]. The mechanisms of the colouration of rutile pigments change with the type of chromophore ion (Cr, Mn, Ni or V) and counter-ion (Nb, Sb, W), varying from yellow to brown [33].

Blue colours

The blue samples 20H and 21H were cobalt-based, showing a considerable amount of Co in their composition. The diffraction pattern of both colourants before and after firing showed a similar pattern to olivine (Table 3). Cobalt silicate olivine has already been identified in 17th century Portuguese azulejos by Raman spectroscopy [4] and is still a common blue ceramic colourant [21]. The main difference between the two pigments was the presence of lead in pigment 21H, which may have been added as flux. Observing the reflectance spectra of samples 20H and 21H (Figure 6), as expected, the blue colour of both colourants and glaze was due to the presence of cobalt. All spectra presented the characteristic triple absorption bands of the Co^{2+} ion at around 530, 600 and 645 nm, commonly observed when Co^{2+} is dissolved in a glass matrix [30, 34]. Two additional absorption bands are observed at around 500 and 760 nm in both pigments before firing (Figure 6, 20H and 21H), but they disappeared after firing (Figure 6), 20H_AF and 21H_AF). These two bands at 500 nm and 760 nm have been attributed to 4T1(F) → 4T2(P) and 4T1(F) → 4A2(F) of the Co^{2+} ion in Co-olivine [35]. Their reflectance spectra changed significantly with the firing. The bands at 500 nm and 760 nm disappeared, while the remaining bands broadened. This could be explained by the partial disappearance of the olivine structure

and the dissolution of the cobalt into the glassy matrix, as corroborated by XRD (Table 3). Pigment 15BCW had a totally different composition, as identified by h-XRF: Si, V and Zr (Table 2). Its components constitute a solid solution of tetravalent vanadium in the zircon lattice (V^{4+}±$ZrSiO_4$) [36], as confirmed through the identification of zircon by XRD. According to previous studies of this pigment, vanadium acts both as a chromophore and a mineraliser forzircon synthesis, allowing it to be formed at lower temperatures and within a narrower temperature range [36]. Concerning sample 15BCW, the reflectance spectra presented absorption bands at 640 nm and 780 nm attributed to V^{4+} in the decahedral and tetrahedral coordination. A band at around 1450 nm assigned to tetrahedral V^{4+} coordination should also exist, but the maximum absorption was out of our analysis range [36-37]. Compared with the traditional azulejos in which cobalt-based colourants were mainly used as blue pigments [9], the studied materials also comprised another type of blue colourant, a vanadium zircon-blue $(Zr,V)SiO_4$.

Violet colour

The violet colourants (18H and 33) were similar in terms of chemical composition with Cr and Sn (Table 2). These elements may indicate a chrome tin cassiterite ($(Sn,Cr)O_2$) pigment, as XRD analysis detected cassiterite in both the raw and fired samples (Table 3). This type of violet pigment can only develop in a narrow range of Cr^{4+} in the cassiterite structure [22]. The pigment is obtained by calcination at high temperatures of tin (IV) oxide and chromium (III) oxide. In Figure 6, it is possible to observe the reflectance spectra of the colourant 18H. A maximum absorption in the 550 nm region can be assigned $^3T_1$-$^3T_2$ transition of Cr^{4+} in the octahedral sites [22, 38]. These samples also had a small amount of cobalt in their composition, which was detected in the elemental analysis, but not by HSI. In contrast, sample 19H was violet due to the cobalt element with an olivine structure, presenting before firing the characteristic Co^{2+} absorption bands of olivine [35] and the Co^{2+} triple band of cobalt commonly observed in a glassy matrix [30, 34] (Figure 6). After firing, sample 19H presented no mineral phase related to the pigment and only the Co^{2+} triple band of cobalt at around 530, 600 and 645 nm, as observed in blue colourant 20H.

Green colour

The green colours were chromium-based colourants (5W, 13BCW, 26H, 31CH). eskolaite (Cr_2O_3) was identified on pigment 5W and 13BCW before firing, and absorption bands at around 460 nm, 600 nm and a shoulder at around 715 nm, attributed to the Cr^{+3} ion in the octahedral coordination, could also be identified in the reflectance spectra. These bands can be attributed to the transitions $^4A_{2g}$-$^4T_{1g}$, $^4A_{2g}$-$^4T_{2g}$ and $^4A_{2g}$-$^2T_{1g}$, $^2E_{2g,}$ respectively [39]. Chromium green pigments were introduced during the nineteenth century and present high thermal stability [17, 39], with eskolaite used to produce green colours by important ceramic manufacturers such as the Sèvres Ceramic Manufactory [17]. Sample 5W showed a lighter green colour compared with 13BCW. Quartz and kaolinite were detected in its mineralogical profile before firing (Table 3). The addition of calcium carbonate, quartz, kaolin or porcelain paste has been previously reported in Sèvres porcelain production to achieve lighter colours [17]. Cobalt-based compounds were mixed with eskolaite to achieve a bluish tonality, as was visible in the reflectance spectra of sample 26H. Colourant 6W presented a very light colour before and after firing. The pigment described as Crystalline Green presented Cr and Cu in its composition, but did not result in a green colour after firing. Pigment 24H, named Jade Green, had a different formulation with Si, V and Zr (Table 3) characteristic of the vanadium zircon pigments already described in sample 15BCW. The reflectance spectra presented an entirely different absorption behaviour compared to the other green samples, with absorption bands at around 640 and 800 nm, attributed to V^{4+} decahedral and tetrahedral coordination [36], as in the blue sample 15BCW.

Red and pink colours

The red pigments are mostly cadmium sulphide and sulphoselenides (8W, 11W, 28H and 29CH), only 14BCW is a Cr-Sn type (Table 3). Cadmium sulphoselenides were first commercialised in 1910 with a production process based on the calcination at about 600 °C of a mixture of cadmium sulfide, selenium, and sulphur [40]. These pigments are composed of ternary CdSeS – solid solutions, which depending on the substitution rate of S by Se, can shift from orange to red colours [19]. Cadmium sulphoselenide pigments are called semiconductors because their source of absorption is electron transitions across the band gap. Therefore, the reflectance spectra of the studied red colourants presented characteristic semiconductor band, as shown in Figure 6. After firing, none of the Cd-Se-based pigments presented the expected colour. It is known that these colours are difficult to achieve and depend on several factors, such as temperature and reductive conditions [19]. Therefore, the selected glaze or firing conditions may not have been appropriate for these pigments. Sample 14BCW had Sn and Cr in its compositions, being a malayaite structure detected by XRD (Table 3). Chromium-doped malayite ($CaSnSiO_5$) structures are produced through the substitution of mostly Sn ions by Cr [18, 38, 41]. The spectral features showed maximum absorption at around 520 nm, which was related to Cr^{4+} in an octahedral site [38].

Similar colourants were identified in the pink samples, 9W and 23H which were identified as chromium-doped malayaite pigments. (Table 3). Chromium-doped tin-based pigments have been [42] used for a long time to colour porcelain glazes. Sample 22H was different from these two pink samples, being identified as Mn-doped alumina corundum pigment, due to the identification of Al and Mn by h-XRF and the corundum structure confirmed by XRD (Table 3). The colour resulted from Mn^{3+} in the structure, with spectral features similar to thoses observed in the literature [43].

Yellow and orange colours

Three types of yellow colours were found in the studied samples: Sb-Pb (10W and 27H), Cd-Se-S (17H) and Sn-V (32) (Table 3). The elemental analysis of the ceramic colourants 10W and 27H showed a high concentration of Pb, Sn and Sb (Table 3), with lead antimonate (bindheimite) identified by XRD before and after firing. The reflectance spectra of these samples, with sample 10W as an example in Figure 6, present the corresponding band gap at around 530 nm (the middle point), which is typical of this type of pigment [13, 44-45]. Lead antimonate yellow ($Pb_2Sb_2O_7$), also known as Naples yellow, is an ancient synthetic pigment that has been produced since antiquity in Middle Eastern ceramic and glass manufacturing [46]. The yellow sample 17H is attributed to a cadmium sulfoselenide compound. With XRF it was possible to identify Cd and Se, which were probably used to produce a more orange tonality. However, S was difficult to detect due to the high amount of Pb overlaping the energy peak of sulphur. After firing, the expected yellow colour was not obtained, coincident to what was observed for the red Cd-S-Se pigments. Finally, pigment 32 was a Sn-V ($SnO_2.V_2O_5$) yellow cassiterite (Table 3). These pigments are based on tin vanadate (SnO_2–V_2O_5) formed by colloidal vanadium particles in a tin oxide matrix [47]. The reflectance spectrum was compatible with that observed in Sn-V systems, where the absorption is attributed to a metal-oxygen charge transfer between O^{2-} and V^{5+} ions [47].

Two of the raw materials were not colourants: 3W was a vanadium (V) oxide in the form of shcherbinaite and sample 7W was an aventurine glaze (Table 3). Vanadium oxide can be mixed with other compounds, such as tin and zirconia, to produce other colours, but vanadium due to its fusing properties can also be used to produce a "sink effect" [13], such as was observed on the fired tile produced in this study (Figure 5). Although mainly colourants were studied, Tijomel, azulejo production was renown by the use of glazes with original tridimensional decorative effects, which would deserve to be further investigated.

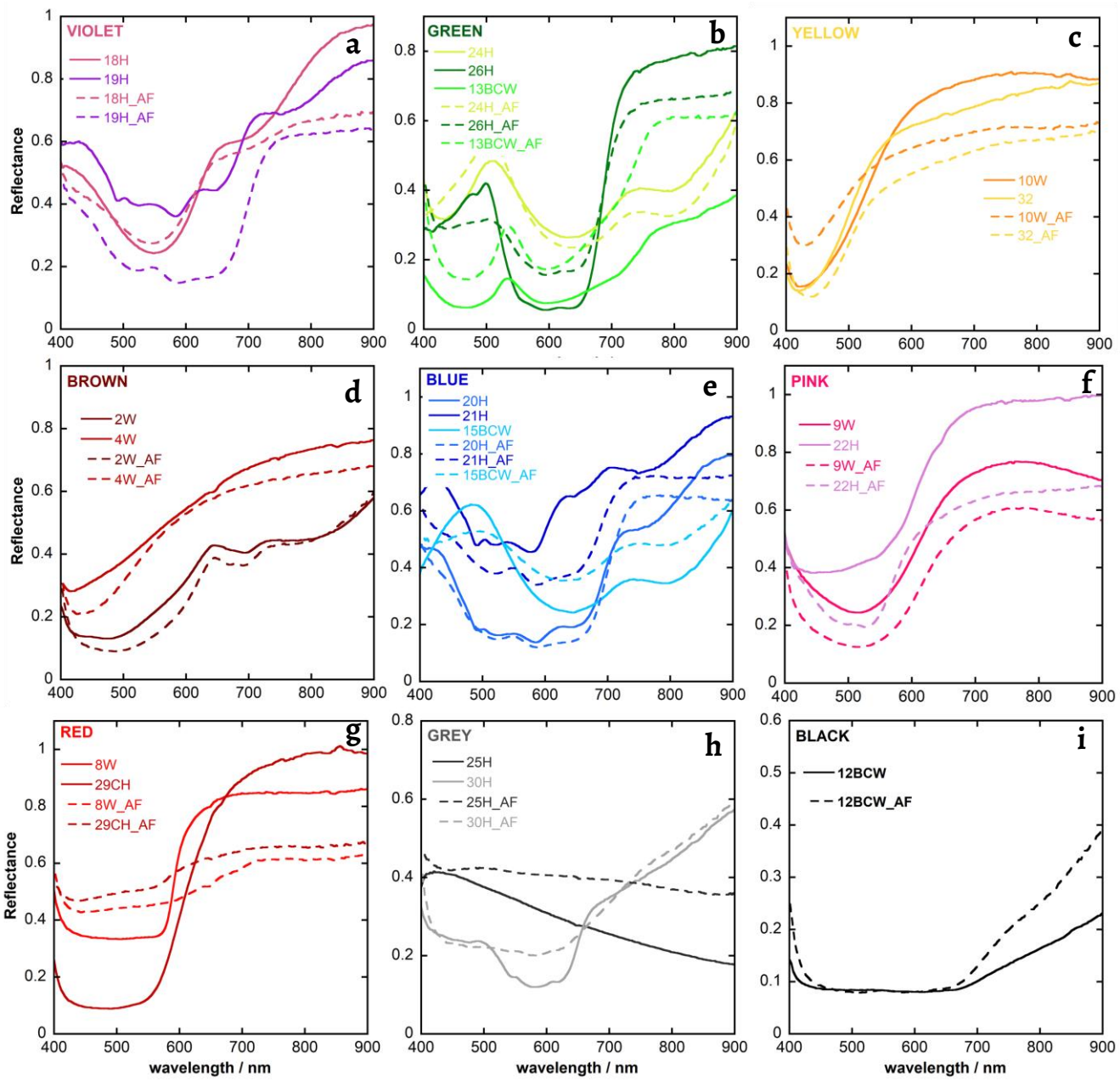

Figure 6. Reflectance spectra of different colourants (full line)before and after being applied in a glazed tile and fired at 980 °C (dashed line): *a)* violet; *b)* green; *c)* yellow; *d)* brown; *e)* blue; *f)* pink; *g)* red; *h)* grey; *i)* black.

The studied materials presented a wide range of colourants: V-Zr and Co blues; Cr-rutile and Cr-Fe-Zn brown spinel; Cr-Co-Zn spinels, Cr and V-Zr greens; Mn-Fe-Ni-Co spinels for black and greys; Cr-mayalite and S-Cd-Se reds; Cr-mayalite and Mn-corundum pinks; Cr-cassiterite and Co violets; and Sb-Pb and V-Sn yellow pigments. Finally, results showed that identifying the pigment after firing was more difficult, mainly due to the zircon opacifier in the selected glaze.

Comparison with azulejos from the Decormel Catalogue

XRF analysis of the glazed tiles from the Decormel Catalogue showed, in general, an elemental composition comprising Al, Si, K, Ca, Ti, Fe, and Pb that may correspond to a lead-silicate glaze composition. In some of these glazes a high peak of Zr was detected, indicating that zircon (identified by XRD) was used as the glaze opacifier (Table 2).

The grey (28, 39) and black (72) azulejos had a composition rich in the transition metals Cr-Mn-Fe-Zn as detected in the black and grey colourants (Table 2). The reflectance spectra

indicated absorption in most of the visible range. In the grey shades the white colourant addition caused higher reflectance values, as previously described for samples 16H, 25H and 30CH (Figure 7).

The brown-orange colourant used in azulejo 194 is similar to pigment 2W. High proportions of Cr, Fe and Zn were detected in its elemental composition and a spinel structure was detected by XRD (Table 2). The results also coincident regarding the spectral features (Figure 6 and Figure 7). Azulejo 155 had a speckled colour of brown and yellow in a mixture of two different colourants Sb-Pb yellow and Cr-Fe-Zn brown.

The blue-coloured azulejo 45 had V and Zr in its composition (Table 2) and zircon was detected by XRD (Table 3), as in the previously described green colourant. Due to the low V concentration, the colouring element was only confirmed by analysing the spectral features that showed absorption bands at 640 nm and 780 nm attributed to V^{4+} decahedral and tetrahedral coordination [36]. In azulejo 116, a broad band may be attributed to the presence of Cu (detected by XRF). The chemical composition of azulejo 178 showed a high peak of cobalt, unlike the other azulejos (Table 2). The spectral feature could be related to the triple cobalt bands of Co^{2+}, although the spectra were poorly defined, probably due to saturation caused by the dark colour (Figure 7). Tin was detected on all the blue glazes, and had been added as an opacifier in the form of cassiterite (Table 3).

The green-coloured azulejos 10 and 187 presented a high Cr peak, and eskolaite was detected by XRD. The spectral features of azulejo 187 had a strong resemblance to the spectra of the raw materials 5W and 13BCW, with absorption bands at around 460 nm, 600 nm and 715 nm previously related to eskolaite (Cr_2O_3) [39]. On the contrary Azulejo 10 presented different absorption bands at around 430, 620 and 650 nm which may indicate the dissolution of the Cr^{3+} into the glass matrix [30]. The green azulejo 19 presented a high peak of Cu and a small peak of Co; however no specific compound was detected by XRD. The reflectance spectra showed a broad band between 600 and 900 nm, which may correspond to the wide single band of Cu^{2+} ions formed due to electronic transition $^2E \rightarrow {}^2T_2$ (790 nm) of the $3d^9$ electronic configuration of the octahedral coordination [30]. None of the Tijomel supplied colourants presented this composition nor spectral features. The green colour of azulejo 48 may be related to a V-Zr pigment, as both these elements were detected by XRF (Table 2), and zirconia was detected by XRD (Table 3). The spectral features are analogous to the supplied sample 24H with absorption bands at around 640 and 800 nm attributed to the V^{4+}ion [36].

In the red-brown glaze of azulejo 25, besides the elements related to the glaze composition of Sn, a small peak of Cr was also detected. Several of the studied red-pink colourants, such as 9W and 23H showed a similar elemental composition and spectral features (Figure 7) identified as malayite ($CaSnOSiO_4$) by XRD (Table 3).

The yellow glaze of azulejo 14 showed high concentrations of Pb, Sn, Sb and Zn that can be associated with lead-antimony and/or lead-tin-antimony yellow pigments traditionally applied in Portuguese azulejo production [4, 6, 48]. The elemental analysis of some yellow colourants, such as 10W also presented high Pb, Sn and Sb concentrations. In both azulejos bindheimite and cassiterite were identified by XRD (Table 3). The spectral features showed similarities with sample 10W (Figure 7). The light-yellow glaze of azulejo 42 seems to be related to the V-Sn yellow pigment, as observed in sample 32. Only zircon, quartz and cassiterite were detected by XRD, and the spectral features were comparable to sample 32 (Figure 6).

In Figure 8 the ab colour coordinates of the different samples can be observed to compare the chromatic colours without the influence of the lightness L coordinate. When compared, the colour coordinates between the ceramic colourants applied on the tile showed some overlap between similar pigments, as, for example, in the cases of the brown-orange spinels in sample 2W and azulejo194, Co-blue in 21H with azulejo 178 and Fab_Azul, V-Zr green 15BCW and azulejo 45, black 12BCW and azulejo 72, and grey 30H and azulejos 28 and 39.

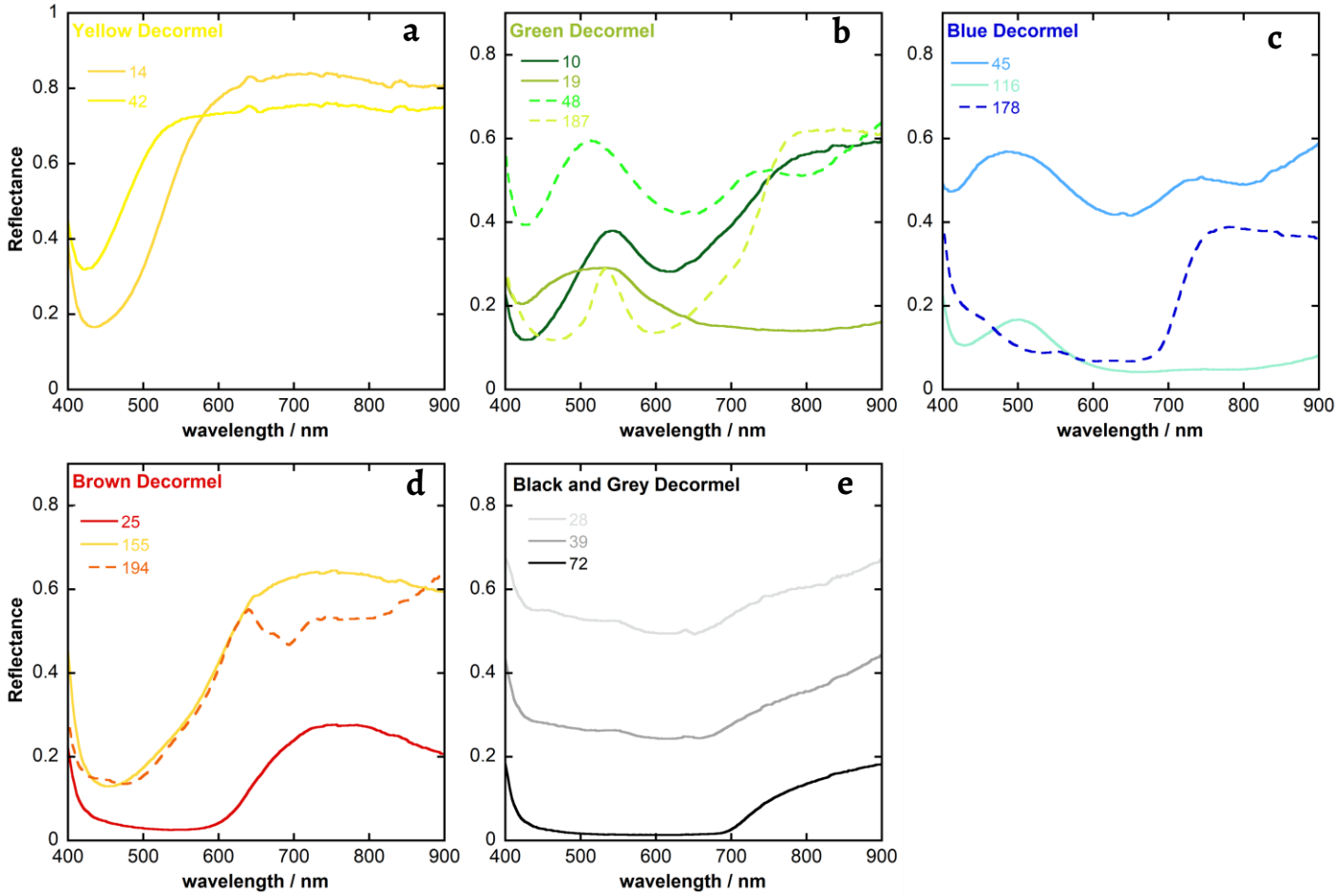

Figure 7. Reflectance spectra of the Tijomel azulejos from the Decormel Catalogue different colour: *a)* yellow; *b)* green; *c)* blue; *d)* brown; *e)* black and grey.

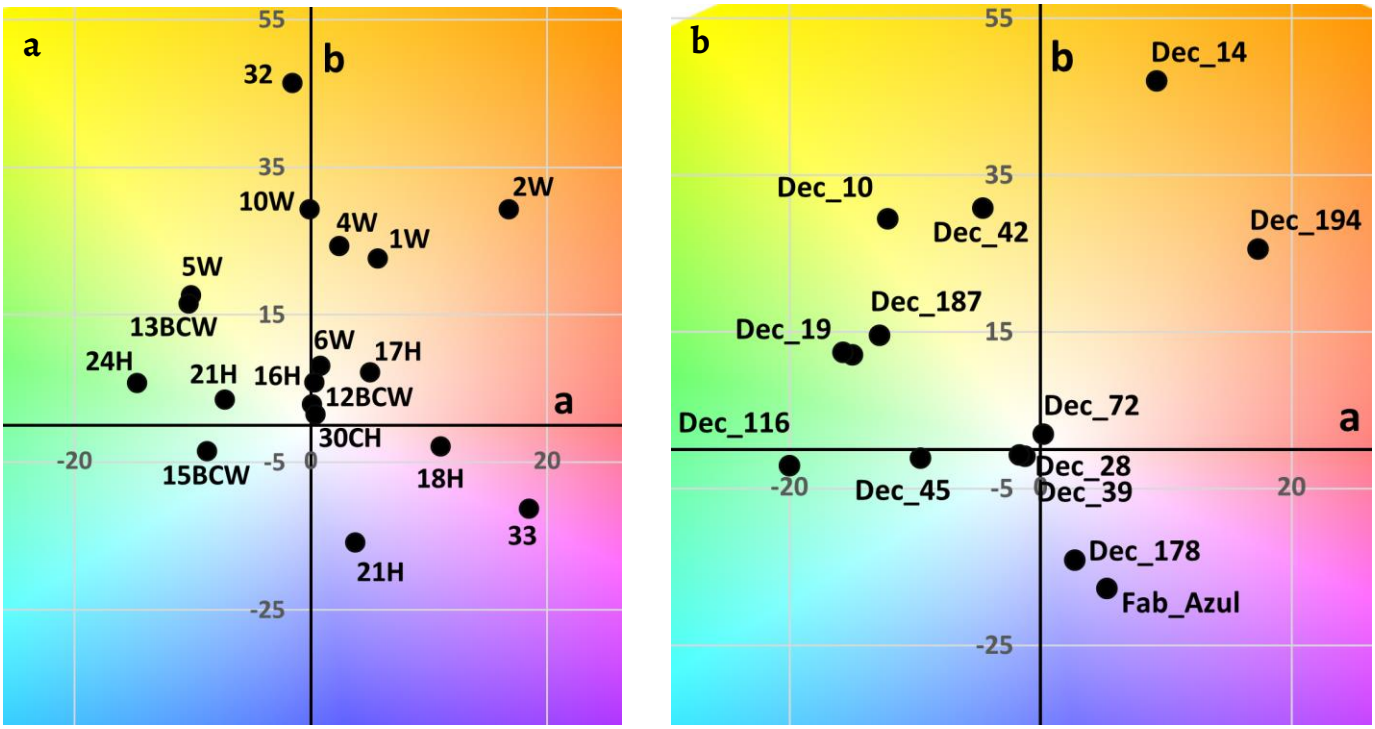

Figure 8. Graphical representation of the obtained colour coordinates a* vs b*: *a)* colourants applied in white tile after firing; *b)* glazes of the azulejos from the Decormel catalogue.

The comparison of the colourants of the discovered raw materials with the azulejos from the Decormel Catalogue showed a good match between the types of pigments, although no direct conclusion can be drawn regarding the use of this specific set of pigments in the azulejos. The Tijomel production showcased in the Decormel Catalogue presented several colourants: brown Cr-Fe-Zn spinels, Co-blue, V-Zr blue and green, Cu green, Cr Green, Cr-mayalite red-brown, Pb-Sb and V-Sn yellows, Cr-Co-Mn-Fe-Zn spinels for black and grey colours and Zr-Si white. To better characterise Tijomel production, further analysis of the glaze composition and microstructure still needs to be performed.

Conclusions

Characterising post-industrial/twentieth-century ceramic colourants and azulejos is more challenging than characterising traditional azulejos due to the wider variety of colourants. This study highlights the importance of firing ceramic colourant materials to enable future comparison with the colourants present in glazed heritage ceramics. The information provided about the material suppliers available for the Portuguese ceramic industry during this period, showed that a wide range of materials were available. Although some pigments were acquired from Portuguese companies, they were mainly obtained by specialist foreign producing companies. Finally, the results showed that the Tijomel production combined traditional azulejo ceramic colourants with more recent compositions. To fully characterise the Tijomel production, further analysis should be performed by testing the raw materials in other types of glazes and firing conditions, as well as, investigating the microstructure of the azulejos.

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